

This invention relates to a catalyst for hydrocracking feedstocks that contain hydrocarbon, whereby said catalyst comprises at least one zeolite Y that is at least partially dealuminified, at least one matrix that is selected from the group that is formed by the mineral matrices, preferably of oxide type, preferably amorphous or poorly crystallized and generally porous, at least one mixed sulfide phase that comprises sulfur and at least one element of group VB of the periodic table (group 5 according to the new notation of the periodic table, Handbook of Chemistry and Physics, 76th edition, 1995-1996, first inside cover page), such as tantalum, niobium and vanadium, preferably niobium as well as at least one element of group VIB of said classification (group 6), such as chromium, molybdenum or tungsten, preferably molybdenum and tungsten, even more preferably molybdenum. Said catalyst also comprises at least one metal of group VIII of said classification (groups 8, 9 and 10), such as iron, cobalt, nickel, ruthenium, osmium, rhodium, iridium, palladium, platinum and optionally at least one element that is selected from the group that is formed by silicon, boron or phosphorus, and optionally at least one element of group VIIA of said classification (group 17), such as fluorine, chlorine, bromine or iodine, preferably fluorine.

This invention also relates to the processes for preparation of said catalyst, as well as its use for hydrocracking feedstocks that contain hydrocarbon such as petroleum fractions, the fractions that are obtained from the carbon that contains aromatic and/or olefinic and/or naphthenic and/or paraffinic

compounds, whereby said feedstocks optionally contain metals, and/or nitrogen and/or oxygen and/or sulfur.

The hydrocracking of heavy petroleum fractions is a very important refining process that makes it possible to produce, from excess heavy feedstocks that cannot be readily upgraded, lighter fractions, such as gasolines, jet fuels and light gas oils that the refiner seeks to adapt his production to the structure of the demand. Some hydrocracking processes make it possible also to obtain a highly purified residue that can constitute excellent bases for oils. Relative to catalytic cracking, the advantage of the catalytic hydrocracking is to provide middle distillates, jet fuels and gas oils of very good quality. The gasoline that is produced has a much lower octane number than the one that is obtained from catalytic cracking.

The catalysts that are used in hydrocracking are all of bifunctional type combining an acid function with a hydrogenating function. The acid function is provided by large-surface substrates (150 to $800 \text{ m}^2\cdot\text{g}^{-1}$ generally) that have a surface acidity, such as halogenated (particularly chlorinated or fluorinated) aluminas, combinations of boron and aluminum oxides, amorphous silica-aluminas and clays. The hydrogenating function is provided either by one or more metals of group VIII of the periodic table, such as iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium and platinum, or by a combination of at least one metal of group VI of the periodic table, such as molybdenum and tungsten and at least one metal of group VIII.

The equilibrium between the two acid and hydrogenating functions is the basic parameter that controls the activity and the selectivity of the catalyst. A weak acid function and a strong hydrogenating function provide catalysts that are not very active and that work at a generally elevated temperature (greater than or equal to 390°C) and at a low feed volumetric flow rate (the VVH that is expressed by volume of feedstock to be treated per unit of volume of catalyst and per hour is generally less than or equal to 2), but provided with a very good selectivity of middle distillates. Conversely, a strong acid function and a weak hydrogenating function provide active catalysts but have poorer selectivities of middle distillates. The search for a suitable catalyst will therefore be centered on a judicious selection of each of the functions to adjust the activity/selectivity pair of the catalyst.

It is thus one of the great advantages of hydrocracking to offer high flexibility at various levels: flexibility as far as the catalysts that are used are concerned, which ensures flexibility of the feedstocks that are to be treated and as far as the products that are obtained are concerned. An easy parameter to control is the acidity of the substrate of the catalyst.

The conventional catalysts of the catalytic hydrocracking consist of, for the large majority, weakly acidic substrates, such as amorphous silica-aluminas, for example. These systems are more particularly used for producing middle distillates of

very good quality, and also, when their acidity is very low, oil bases.

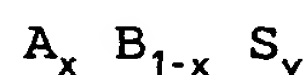
In the substrates that are not very acidic is found the family of amorphous silica-aluminas. Many hydrocracking market catalysts have a combined silica-alumina base, either with a metal of group VIII or preferably when the contents of heteroatomic poisons of the feedstock that is to be treated exceed 0.5% by weight, with a combination of sulfides of the metals of groups VIB and VIII. These systems have a very good selectivity of middle distillates, and the products that are formed are of good quality. These catalysts, for the less acidic among them, can also produce lubricating bases. The drawback of all of these catalytic systems with an amorphous substrate base is, as has been said, their weak activity.

In contrast, single sulfides of elements of group VB have been described as components of hydrorefining catalysts of feedstocks that contain hydrocarbon, such as, for example, the niobium trisulfide in Patent US-A-5,294,333. Mixtures of single sulfides that comprise at least one element of group VB and one element of group VIB or of group VIII have also been tested as components of hydrorefining catalysts of feedstocks that contain hydrocarbon, such as, for example, in Patent US-A-4,871,445, Patent US-A-4,910,181 or Patent US-A-5,275,994.

The research work that has been carried out by the applicant on zeolites and hydrogenating active phases led him to discover that, surprisingly enough, a catalyst for hydrocracking feedstocks that contain hydrocarbon comprises at least one matrix

that is selected from the group that is formed by mineral matrices that are preferably of oxide type, preferably amorphous or poorly crystallized and generally porous, such as alumina, at least one zeolite Y that is at least partially dealuminified, and at least one mixed sulfide phase. This catalyst also contains at least one element of group VIII and optionally an element that is selected from the group that is formed by silicon, phosphorus and boron, optionally at least one element that is selected from group VIIA.

The mixed sulfide phase that is present in the catalyst according to the invention is characterized by the following approximate general formula:



where:

- x is a number between 0.001 and 0.999, preferably between 0.005 and 0.995, more preferably between 0.05 and 0.95,
- y is a number between 0.1 and 8, and preferably between 0.1 and 6, and even more preferably between 0.5 and 4,
- A is an element of group VB, such as tantalum, niobium or vanadium, preferably niobium,
- B is an element that is selected from group VIB, such as chromium, molybdenum or tungsten, preferably molybdenum or tungsten, even more preferably molybdenum.

The catalyst according to the invention is in supported form, i.e., it comprises at least one substrate that consists of at least one matrix, for example of oxide type, for example

alumina, and at least one zeolite Y that is at least partially dealuminified.

The catalyst according to this invention generally contains in % by weight relative to the total mass of the catalyst:

-- 0.1 to 99.9%, preferably 1 to 99.5% and even more preferably 5 to 99.0% of at least one matrix, preferably of oxide type, preferably amorphous or poorly crystallized and generally porous,

-- 0.1 to 99.8%, preferably 0.1 to 90% and even more preferably 0.1 to 80% and very preferably 0.1 to 70% of at least one zeolite Y that is at least partially dealuminified, whose mesh parameter is between 2.424 nm and 2.455 nm or 24.55 Å (1 Å is equal to 10^{-10} m, or 0.1 nm), preferably between 2.426 nm and 2.438 nm, and whose overall $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio is greater than 8, preferably greater than 10, more preferably greater than 15, and very preferably greater than 20,

-- 0.1 to 99.5%, preferably 0.5 to 99% and even more preferably 1 to 90% of at least one mixed sulfide phase of at least one element of group VB and at least one element of group VIB,

whereby the catalyst can also contain:

-- from 0.1 to 20% of at least one metal of group VIII,

-- from 0 to 20%, preferably 0 to 15%, and more preferably 0.1 to 15% of at least one element that is selected from the group that is formed by boron, phosphorus and silicon, and

-- from 0 to 15%, preferably 0.1 to 15% and more preferably from 0.1 to 10% of at least one element that is selected from group VIIA, preferably fluorine.

The matrix is preferably selected from the group that is formed by the mineral matrices, preferably the porous mineral matrices, preferably amorphous or poorly crystallized and preferably of oxide type.

Identification of the mixed sulfide phase is done generally from the x-ray diffraction diagram. It can also be done from the determination of the metal-metal distance that is measured by the x-ray absorption technique or "Extended X-Ray Absorption Fine Structure" (EXAFS). For example, in the case of a mixed molybdenum and niobium sulfide, identification by the EXAFS method is done by determination of niobium-niobium distances or niobium-molybdenum distances if the EXAFS analysis is carried out at threshold K of niobium. It can also be done by the determination of the molybdenum-molybdenum and molybdenum-niobium distances if the EXAFS analysis is carried out at threshold K of molybdenum.

The X diffraction diagram is obtained with an INEL diffractometer with a curved multidetector by using the standard method of powders with the alpha 1 K monochromatic radiation of copper. From the position of the diffraction peaks that is shown by angle 2 theta, reticular distances d_{hkl} that are characteristic of the sample and the mesh parameters of mixed phase a and c at Å ($1 \text{ Å} = 1 \text{ angstrom} = 10^{-10} \text{ m}$) are calculated by Bragg's equation. Mesh parameter "a" represents the metal-metal mean distance

between two closely related ions and is characteristic of the existence of a mixed phase. It is also possible to determine the type of structure by diffraction. Thus, for example, in the case of a mixed molybdenum and niobium sulfide, the single sulfides of Mo and Nb, MoS_2 and NbS_2 both exist in the form of two types of structure, hexagonal shape 2s and rhombohedral shape 3s. For the molybdenum-rich samples ($x < 0.5$), the mixed phase tends to crystallize in hexagonal structure type 2s, and the mesh parameters vary linearly based on the proportion of niobium of the mixed phase as Table 1 shows it. For the niobium-rich samples ($x \geq 0.5$), the mixed phase tends to crystallize in the rhombohedral structure 3s, and the mesh parameters also vary linearly based on the niobium composition as Table 2 shows it.

The estimation of the measuring error $\Delta(d_{hkl})$ to d_{hkl} is calculated, based on the absolute error that is assigned to the measurement of the angle 2θ , by Bragg's equation. An absolute error $\Delta(2\theta)$ that is equal to $\pm 0.05^\circ$ is ordinarily accepted. Intensity I_{rel} that is assigned to each d_{hkl} value is measured according to the surface area of the corresponding diffraction peak.

TABLE 1

| Phase | a (Å) | c (Å) |
|--|-------|-------|
| MoS ₂ -2s | 3.16 | 12.29 |
| Nb _{0.2} Mo _{0.8} S ₂ | 3.20 | 12.05 |
| Nb _{0.3} Mo _{0.5} S ₂ | 3.20 | 12.02 |
| Nb _{0.4} Mo _{0.6} S ₂ | 3.25 | 12.00 |
| NbS ₂ -2s | 3.31 | 11.89 |

TABLE 2

| Phase | a (Å) | c (Å) |
|--|-------|-------|
| MoS ₂ -3s | 3.16 | 18.37 |
| Nb _{0.6} Mo _{0.6} S ₂ | 3.25 | 18.00 |
| Nb _{0.7} Mo _{0.3} S ₂ | 3.27 | 17.98 |
| Nb _{0.3} Mo _{0.2} S ₂ | 3.30 | 17.97 |
| NbS ₂ -3s | 3.33 | 17.81 |

The analysis of the X-ray diffraction diagram in the form of mesh parameters that are presented in Tables 1 and 2 makes it possible to identify the mixed niobium and molybdenum sulfide.

The analysis by the EXAFS technique is carried out at threshold K of niobium with the synchrotron radiation between 18850 and 19800 eV by measuring the intensity that is absorbed by a powder sample that is deposited on adhesive tape. The absorption spectrum is analyzed according to an established

procedure (F. W. Lyttle, D. E. Sayers and E. A. Stern, Physical Review B, Vol. 11, page 4825, 1975 and E. A. Stern, D. E. Sayers and F. W. Lyttle, Physical Review B, Vol. 11, page 4836) which makes it possible to determine the interatomic distances.

The analysis of the x-ray adsorption spectrum makes it possible to deduce a radial distribution function. This radial distribution shows a first peak relative to the sulfur-containing environment of niobium and whose position of the maximum provides the niobium-sulfur distance or R_1 in general of 2.45 to 2.48 Å, typical of NbS_2 . Then observed in this radial distribution is a second peak that corresponds to the second sphere of coordination of niobium that consists of niobium atoms or molybdenum atoms that cannot be distinguished because of their very closely related atomic numbers and whose position of the maximum provides the metal-metal (niobium-niobium or niobium-molybdenum) R_2 mean distance whose value varies based on the composition of the mixed phase as Table 3 shows it; said value is between the values of the niobium-niobium distance in NbS_2 (3.33 Å) and the molybdenum-molybdenum distance in MoS_2 (3.16 Å), and it is generally on an average of 3.20 to 3.35 Å. This distance is consistent with the distances that are to be determined by X diffraction and varies with the composition of the mixed phase. The distances that are recorded in Table 3 are corrected by phase shift and can therefore be compared to data that are obtained by X diffraction. The determination of the metal-metal interatomic distances by the EXAFS technique is very specific since the estimation of the absolute error on the distance is equal to ± 0.02 Å.

TABLE 3

| Phase | R1 (Å) | R2 (Å) |
|--|--------|--------|
| $\text{Nb}_{0.2}\text{Mo}_{0.8}\text{S}_2$ | 2.46 | 3.20 |
| $\text{Nb}_{0.3}\text{Mo}_{0.7}\text{S}_2$ | 2.45 | 3.22 |
| $\text{Nb}_{0.4}\text{Mo}_{0.6}\text{S}_2$ | 2.48 | 3.27 |
| $\text{Nb}_{0.6}\text{Mo}_{0.4}\text{S}_2$ | 2.47 | 3.28 |
| $\text{Nb}_{0.7}\text{Mo}_{0.3}\text{S}_2$ | 2.48 | 3.30 |
| $\text{Nb}_{0.8}\text{Mo}_{0.2}\text{S}_2$ | 2.48 | 3.31 |
| NbS_2 | 2.48 | 3.33 |

The catalyst according to the invention can be prepared either by preparing in a first step a bulk mixed sulfide phase and by depositing it then on a substrate, or by directly producing a precursor of the catalyst that consists of a supported mixed sulfide phase. The elements of group VIII as well as elements that are selected from the group that is formed by silicon, phosphorus and boron, and the elements of group VIIA can be introduced at any stage of the preparation, for example during the preparation of the bulk or supported mixed sulfide phase, or else on the substrate alone.

A preferred process of preparation of the bulk mixed sulfide phase in the catalyst according to this invention comprises the following stages:

a) A reaction mixture that contains at least the following compounds is formed: at least one element source of group VB, at least one element source of group VIB, at least one source of an

element that is selected from the group that is formed by the elements of group VIII, optionally water, optionally at least one source of an element that is selected from the group that is formed by silicon, phosphorus and boron, optionally an element that is selected from among the halogens, i.e., the elements of group VIIA, preferably fluorine,

b) said mixture is kept at a heating temperature that is generally greater than about 40°C, at a pressure that is at least equal to the atmospheric pressure and in the presence of a sulfur compound until said mixed sulfide phase is obtained.

The mixture that is produced in stage a) above can be carried out simultaneously or successively, the order insignificant, in the same physical space or separately.

Stage b) proves to be very difficult for most of the standard sulfurization methods that are known to one skilled in the art.

Actually, the sulfurization of the solids that contain at least one element of group VB in oxide form proves to be very difficult by most of the standard sulfurization methods that are known to one skilled in the art. The catalysts that contain at least one element of group VB that is supported on an alumina-type matrix are known for being very difficult to sulfurize, once the element combination of the group VB-matrix has been calcined at a temperature that is greater than 200°C.

A preferred method according to the invention consists in not calcining the catalyst and in initiating sulfurization by a gaseous compound that comprises sulfur, such as CS₂, in a

pressurized autoclave. Thus, a preferred method according to the invention consists in initiating the sulfurization of the mixture, generally in the form of powdered solids, at a temperature of between 40 and 700°C, preferably between 60 and 500°C, under autogenous pressure and in the presence of a gaseous sulfur compound such as preferably CS₂.

An autoclave that is coated on the inside with a polymer material, in general polytetrafluoroethylene, is preferably used at a temperature that is greater than 100°C. The heating period of the reaction mixture that is necessary for sulfurization depends on the composition of the reaction mixture and the reaction temperature. Such a method that is described in the literature for the synthesis of a catalyst that comprises niobium sulfide on alumina (Journal of Catalysis, Vol. 156, pages 279-289 (1995)) and in Patent EP-A-440,516 for the synthesis of a binary sulfur compound, i.e., a single sulfide that comprises sulfur and another element, transition metal or rare earth, was found to be applicable for the synthesis of mixed sulfides according to this invention.

The catalysts that are supported by this invention can be prepared by any method that is known to one skilled in the art. Some of the possible preparation methods are described below.

In general, it is possible to mix mechanically the dealuminified zeolite Y and the matrix that is generally in powder form with any precursor of the mixed sulfide phase, then to initiate sulfurization, as it is described in more detail below. It is also possible to carry out a mechanical mixing that

comprises, on the one hand, powder of the mixed sulfide that is synthesized according to one of the methods that are described above, and, on the other hand, the substrate (i.e., a mixture of matrix and zeolite) that is also in powder form, then optionally to initiate shaping.

In all of the cases, it is a priori possible to add optional elements that are present in the catalyst that is supported according to the invention at any stage of the preparation, according to the methods that are known to one skilled in the art.

One of the preferred processes of preparation of the supported mixed sulfide phase in the catalyst according to the invention comprises the following stages:

a) a reaction mixture is formed that contains at least the following compounds: at least one matrix that is selected from the group that is formed by the mineral matrices, preferably of oxide type, preferably amorphous or poorly crystallized and generally porous, at least one zeolite Y, at least partially dealuminified, whose mesh parameter is between 2.424 nm and 2.455 nm, preferably between 2.426 nm and 2.438 nm, and whose overall $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio is greater than 8, preferably greater than 10, more preferably greater than 15, and very preferably greater than 20, at least one element source of group VB, at least one element source of group VIB, at least one element that is selected from the group that is formed by the elements of group VIII, optionally water, optionally at least one source of an element that is selected from the group that is formed by

silicon, phosphorus and boron, optionally at least one source of an element that is selected from among the halogens, i.e., the elements of group VIIA, preferably fluorine,

b) said mixture is kept at a heating temperature that is generally greater than about 40°C in the presence of a sulfur compound until a solid is obtained that contains at least one matrix, at least one dealuminified zeolite Y and at least one mixed sulfide phase.

Stage a) is preferably an impregnation stage of the substrate.

Thus, for example in the preferred case where the metal of group VB is niobium and where the metal of group VIB is molybdenum, it is possible to impregnate the substrate (that comprises the matrix and the zeolite) or the matrix alone, for example of alumina, by ammonium heptamolybdate, to initiate drying at 80°C, then to impregnate by niobium oxalate, to initiate drying at 80°C, and to initiate sulfurization, for example, and preferably by CS₂ in an autoclave under autogenous pressure, as described for the preparation of the bulk mixed sulfide phase, for example at 400°C for 10 hours.

It is also possible to produce the mixture of powders that comprise the element source of group VB, the element source of group VIB, optionally water, optionally the source of the element that is selected from among silicon, phosphorus and boron, optionally the source of the element of group VIIA and optionally the sulfur source and to impregnate the substrate. It is also possible to impregnate the matrix alone and to add zeolite Y

later, by any means that is known to one skilled in the art, for example by mechanical mixing.

When the matrix is impregnated, the impregnation of the matrix is preferably carried out by the so-called "dry" impregnation method that is well known to one skilled in the art. The impregnation can be carried out in a single stage by a solution that contains all of the constituent elements of the final catalyst.

The shaping of the substrate or of the supported catalyst according to the invention can be an extrusion, a pelletizing, the oil-drop method, a turntable granulation or any other method that is well known to one skilled in the art. The preformed substrate is optionally calcined in air, usually at a temperature of at least 300°C, commonly about 350 to 1000°C.

The mixed sulfide phase, like the element of group VIII, like the element that is selected from the group that is formed by P, B and Si and the element that is selected from group VIIA of halides, preferably fluorine, can be introduced into the catalyst at various levels of the preparation and various manners.

The mixed sulfide phase can be introduced in part only (a case of, for example, the combination of at least one metal of group VB and/or group VIB and at least one metal of group VIII) or completely at the time of mixing of the porous matrix, optionally with some or all of the zeolite.

The metal of group VIII like the element that is selected from the group that is formed by P, B, Si and the element that is

selected from among the halides of group VIIA, can be introduced by one or more ion exchange operations in the calcined matrix that consists of mixed sulfide that is dispersed in the selected substrate, with a solution that contains at least one metal precursor salt of group VIII. It can be introduced by at least one impregnation operation of the substrate that is shaped and calcined, by a precursor solution of at least one metal of group VIII (particularly cobalt and/or nickel), whereby any metal precursor of group VIII is preferably introduced at the same time or after any metal precursor of group VB and VIB.

In the case where the metals are introduced in several impregnations, corresponding precursor salts, an intermediate drying stage of the catalyst is generally carried out at a temperature of between 60 and 200°C.

The porous mineral matrix that is usually amorphous or poorly crystallized generally consists of at least one refractory oxide in amorphous or poorly crystallized form. Said matrix is usually selected from the group that is formed by alumina, silica, silica-alumina, or a mixture of at least two of the oxides that are cited above. It is also possible to select the aluminates. It is preferred to use matrices that contain alumina in all of these forms that are known to one skilled in the art, for example gamma-alumina.

Among zeolites Y, it is usually preferred to use zeolites Y whose ratio that is expressed in terms of silicon/aluminum (Si/Al) framework atoms is greater than about 3:1. Zeolites with a faujasite structure, and in particular stabilized zeolites Y

and ultrastabilized zeolites USY, are advantageously used either in hydrogen form or in a form that is partially exchanged with metal cations, for example cations of alkaline metals or alkaline-earth metals and/or cations of rare earth metals of atomic number 57 to 71 inclusive (Zéolithe Molecular Sieves Structure, Chemistry and Uses, D. W. BRECK, J. WILLEY and Sons, 1973).

Dealuminified zeolite Y is characterized by a mesh parameter (crystalline mesh) that is between 2.424 nm and 2.455 nm, preferably between 2.426 nm and 2.438 nm, whose overall $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio is greater than 8, preferably greater than 10, more preferably greater than 15, and very preferably greater than 20.

A dealuminified zeolite Y is preferably used that also has the following properties:

- an $\text{SiO}_2/\text{Al}_2\text{O}_3$ framework molar ratio that is greater than or equal to the overall $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio,
- a content of cations of the alkaline-earth or alkaline metals and/or cations of rare earths (of atomic number 57 to 71 inclusive) such as the atomic ratio $[n \times \text{M}^{n+}]/\text{Al}$ (whereby n is the charge of cation M) is less than 0.8, preferably less than 0.5 and even more preferably less than 0.1,
- a specific surface area that is determined by the B.E.T. method that is greater than about $400 \text{ m}^2/\text{g}$, and preferably greater than $550 \text{ m}^2/\text{g}$
- a water adsorption capacity at 25°C for a P/P_0 value of 0.2, greater than about 6% by weight.

The element sources of group VB that can be used are well known to one skilled in the art. For example, among the niobium sources, it is possible to use oxides, such as dinobium pentaoxide Nb_2O_5 , niobic acid $\text{Nb}_2\text{O}_5 \cdot \text{H}_2\text{O}$, niobium hydroxides and polyoxoniobates, the niobium alkoxides of formula $\text{Nb}(\text{OR}_1)_3$ where R_1 is an alkyl radical, niobium oxalate $\text{NbO}(\text{HC}_2\text{O}_4)_5$, ammonium niobate. Niobium oxalate or ammonium niobate is preferably used.

The element sources of group VIB that can be used are well known to one skilled in the art. For example, among the sources of molybdenum and tungsten, it is possible to use oxides and hydroxides, molybdic acids and tungstic acids and their salts, in particular ammonium salts such as ammonium molybdate, ammonium heptamolybdate, ammonium tungstate, phosphomolybdic acid, phosphotungstic acid and their salts, silicomolybdic acid, silicotungstic acid and their salts. Oxides and ammonium salts such as ammonium molybdate, ammonium heptamolybdate and ammonium tungstate are preferably used.

The sulfur source can be elementary sulfur, carbon sulfide, hydrogen sulfide, sulfur-containing hydrocarbons, such as dimethyl sulfide, dimethyl disulfide, mercaptans, thiophene compounds, thiols, polysulfides such as, for example, ditiononylpolysulfide or TPS-37 of the ATOCHEM Company, sulfur-rich petroleum fractions such as gasoline, kerosene, gasoil, alone or mixed with one of the sulfur-containing compounds that is cited above. The preferred sulfur source is carbon sulfide or hydrogen sulfide.

The preferred phosphorus source is phosphoric acid H_3PO_4 , but its salts and esters such as alkaline phosphates, ammonium phosphates, gallium phosphates or alkyl phosphates are also suitable. The phosphorus can be, for example, introduced in the form of a phosphoric acid mixture and a basic organic compound that contains nitrogen, such as ammonia, primary and secondary amines, cyclic amines, compounds of the pyridine family and quinolines and compounds of the pyrrole family.

Many sources of silicon can be used. Thus, it is possible to use ethyl orthosilicate $\text{Si}(\text{OEt})_4$, siloxanes, polysiloxanes, silicones, silicone emulsions, halide silicates such as ammonium fluorosilicate $(\text{NH}_4)_2\text{SiF}_6$ or sodium fluorosilicate Na_2SiF_6 . Silicomolybdic acid and its salts, silicotungstic acid and its salts can also be advantageously used. The silicon can be added by, for example, impregnation of ethyl silicate in solution in a water/alcohol mixture. The silicon can also be added by, for example, impregnation of a silicon compound of silicone type that is suspended in water.

The boron source can be boric acid, preferably orthoboric acid H_3BO_3 , biborate or ammonium pentaborate, boron oxide, or boric esters. Boron can be, for example, introduced in the form of a boric acid mixture, oxidized water and a basic organic compound that contains nitrogen such as ammonia, primary and secondary amines, cyclic amines, compounds of the family of pyridine and quinolines and compounds of the pyrrole family. Boron can be introduced, for example, with a boric acid solution in a water/alcohol mixture.

The sources of elements of group VIIA that can be used are well known to one skilled in the art. For example, the fluoride anions can be introduced in the form of fluorohydric acid or its salts. These salts are formed with alkaline metals, ammonium or an organic compound. In the latter case, salt is advantageously formed in a reaction mixture by reaction between the organic compound and the fluorohydric acid. It is also possible to use hydrolyzable compounds that can release fluoride anions in water, such as ammonium fluorosilicate $(\text{NH}_4)_2\text{SiF}_6$, silicon tetrafluoride SiF_4 or sodium tetrafluoride Na_2SiF_6 . The fluorine can be introduced by, for example, impregnation of an aqueous solution of hydrofluoric acid or ammonium fluoride.

The catalyst of this invention contains an element of group VIII such as iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium or platinum. Among the metals of group VIII, it is preferred to use a metal that is selected from the group that is formed by iron, cobalt, nickel and ruthenium. Advantageously, the following combinations of metals are used: nickel-niobium-molybdenum, cobalt-niobium-molybdenum, iron-niobium-molybdenum, nickel-niobium-tungsten, cobalt-niobium-tungsten, iron-niobium-tungsten, whereby the preferred combinations are: nickel-niobium-molybdenum, and cobalt-niobium-molybdenum. It is also possible to use combinations of four metals, for example, nickel-cobalt-niobium-molybdenum. It is also possible to use combinations that contain a noble metal such as ruthenium-niobium-molybdenum, or else ruthenium-nickel-niobium-molybdenum.

The impregnation of the molybdenum can be facilitated by adding phosphoric acid into the solutions of ammonium paramolybdate, which makes it possible also to introduce phosphorus to promote catalytic activity. Other compounds of phosphorus can be used as is well known to one skilled in the art.

The catalysts that are obtained by this invention are shaped in the form of grains of different shape and dimensions. They are generally used in the form of cylindrical extrudates or multilobar extrudates, such as bilobar, trilobar or polylobar extrudates of straight or twisted shape, but they can optionally be produced and used in the form of crushed powder, tablets, rings, balls, and wheels. They have a specific surface area that is measured by nitrogen adsorption according to the BET method (Brunauer, Emmett, Teller, J. Am. Chem. Soc., Vol. 60, 309-316 (1938)) of between about 50 and about 600 m²/g, a pore volume that is measured by porosimetry with mercury of between about 0.2 and about 1.5 cm³/g, and a size distribution of pores that can be monomodal, bimodal or polymodal.

The catalysts that are obtained by this invention are used for hydrocracking feedstocks that contain hydrocarbon such as petroleum fractions. The feedstocks that are used in the process are gasolines, kerosenes, gas oils, vacuum gas oils, atmospheric residues, vacuum residues, atmospheric distillates, vacuum distillates, heavy fuels, oils, waxes and paraffins, used oils, residues or crudes that are deasphalted, feedstocks that come from thermal or catalytic conversion processes and their

mixtures. They contain heteroatoms such as sulfur, oxygen and nitrogen and optionally metals.

The catalysts that are thus obtained are advantageously used for hydrocracking particularly heavy hydrocarbon fractions of vacuum distillate type, deasphalted or hydrotreated residues or the equivalent. The heavy fractions preferably consist of at least 80% by volume of compounds whose boiling points are at least 350°C and preferably between 350 and 580°C (i.e., corresponding to compounds that contain at least 15 to 20 carbon atoms). They generally contain heteroatoms such as sulfur and nitrogen. The nitrogen content is usually between 1 and 5000 ppm by weight and the sulfur content is between 0.01 and 5% by weight.

The hydrocracking conditions such as temperature, pressure, hydrogen recycling rate, hourly volumetric flow rate can be very variable based on the nature of the feedstock, the quality of the desired products and installations that the refiner uses. The temperature is generally higher than 200°C and preferably between 250°C and 480°C. The pressure is higher than 0.1 MPa and preferably higher than 1 MPa. The quantity of hydrogen is at least 50 and often between 80 and 5000 normal liters of hydrogen per liter of feedstock. The hourly volumetric flow rate is generally between 0.1 and 20 volumes of feedstock per volume of catalyst and per hour.

The catalysts of this invention are preferably subjected to an additional sulfurization treatment before being used in the hydrocracking reaction. This treatment makes it possible to

transform at least partly the residual metal radicals into sulfide before they are brought into contact with the feedstock that is to be treated. This activation treatment by sulfurization is well known to one skilled in the art and can be carried out by any method that is already described in the literature or in-situ, i.e., in the hydrocracking reactor, or ex-situ.

A standard sulfurization method that is well known to one skilled in the art consists in heating in the presence of hydrogen sulfide at a temperature of between 150 and 800°C, preferably between 250 and 600°C, generally in a flushed-bed reaction zone.

The catalyst of this invention can be advantageously used for hydrocracking vacuum distillate-type fractions that are high in sulfur and nitrogen, more particularly, for example, fractions with a sulfur content that is greater than 0.1% by weight and with a nitrogen content that is greater than 10 ppm.

In a first embodiment or partial hydrocracking that is still called mild hydrocracking, the conversion level is less than 55%. The catalyst according to the invention is then used at a temperature that is generally higher than or equal to 230°C, preferably between 300°C and 480°C, and more preferably between 350°C and 450°C. The pressure that is preferably greater than 2 MPa, more preferably 3 MPa and preferably less than 12 MPa, and more preferably less than 10 MPa. The quantity of hydrogen is at least 100 normal liters of hydrogen per liter of feedstock and preferably between 200 and 3000 normal liters of hydrogen per

liter of feedstock. The hourly volumetric flow rate is preferably between 0.15 and 10 volumes of feedstock per volume of catalyst and per hour. Under these conditions, the catalysts of this invention have a better activity of conversion, hydrodesulfurization and hydrodenitrating than the commercial catalysts.

In a second embodiment, the catalyst of this invention can be used for partial hydrocracking, advantageously under conditions of moderate hydrogen pressure, fractions, for example, of vacuum distillate type that are high in sulfur and nitrogen which were previously hydrotreated. In this hydrocracking mode, the conversion level is less than 55%. In this case, the petroleum fraction conversion process takes place in two stages, whereby the catalysts according to the invention are used in the second stage. The catalyst of the first stage has a hydrotreatment function and comprises a matrix that preferably has an alumina base and that preferably does not contain zeolite, and at least one metal that has a hydrogenating function. Said matrix is an oxide-type amorphous or poorly crystallized porous mineral matrix. By way of nonlimiting example, it is possible to cite aluminas, silicas, and silica-aluminas. It is also possible to select aluminates. It is preferred to use matrices that contain alumina under all of these forms that are known to one skilled in the art and even more preferably aluminas, for example gamma-alumina. The hydrotreatment function is ensured by at least one metal or metal compound of group VIII such as nickel and cobalt in particular. It is possible to use a combination of

at least one metal or metal compound of group VIB (for example molybdenum or tungsten) and at least one metal or metal compound of group VIII (for example cobalt or nickel) of the periodic table. The total concentration of metal oxides of groups VIB and VIII is preferably between 5 and 40% by weight and more preferably between 7 and 30% by weight and the ratio by weight that is expressed in terms of metal oxide (metals) of group VIB to metal oxide (metals) of group VIII is preferably between 1.25 and 20, and more preferably between 2 and 10. In addition, this catalyst can contain phosphorus. The phosphorus content, expressed in concentration of diphosphorus pentaoxide P_2O_5 , will preferably be at most 15%, more preferably between 0.1 and 15% by weight and very preferably between 0.15 and 10% by weight. It is also possible to contain the boron in a B/P ratio that is preferably between 1.05 and 2 (atomic), whereby the sum of the contents of boron (B) and phosphorus (P) that are expressed in terms of oxides is preferably between 5 and 15% by weight.

The first stage generally takes place at a temperature of between 350 and 460°C, preferably between 367 and 450°C, a total pressure of at least 2 MPa, preferably at least 3 MPa, an hourly volumetric flow rate of between 0.1 and 5 volumes of feedstock per volume of catalyst and per hour, preferably between 0.2 and 2 volumes of feedstock per volume of catalyst and per hour and with a quantity of hydrogen of at least 100 normal liters per liter of feedstock, and preferably between 260 and 3000 normal liters per liter of feedstock.

For the conversion stage with the catalyst according to the invention (or second stage), the temperatures are generally greater than or equal to 230°C and often between 300°C and 480°C and preferably between 300 and 450°C. The pressure is generally at least 2 MPa and preferably at least 3 MPa. The quantity of hydrogen is at least 100 liters of hydrogen per liter of feedstock and preferably between 200 and 3000 liters of hydrogen per liter of feedstock. The hourly volumetric flow rate is preferably between 0.15 and 10 volumes of feedstock per volume of catalyst and per hour. Under these conditions, the catalysts of this invention exhibit a better activity in conversion, hydrodesulfurization, hydrodenitrating and a better selectivity of middle distillates than the commercial catalysts. The service life of the catalysts is also improved in the moderate pressure range.

In another embodiment, the catalyst of this invention can be used for hydrocracking under high hydrogen pressure conditions, generally of at least 5 MPa. The treated fractions are, for example, of vacuum distillate type that are high in sulfur and nitrogen and that have been previously hydrotreated. In this hydrocracking mode, the conversion level is greater than 55%. In this case, the petroleum fraction conversion process takes place in two stages, whereby the catalyst according to the invention is used in the second stage.

The catalyst of the first stage has a hydrotreatment function and comprises a matrix that has an alumina base and preferably does not contain zeolite, and at least one metal that

has a hydrogenating function. Said matrix can also consist of, or contain, silica, silica-alumina, boron oxide, magnesia, zirconia, titanium oxide or a combination of these oxides. The hydro-dehydrogenating function is ensured by at least one metal or metal compound of group VIII such as nickel and cobalt in particular. It is possible to use a combination of at least one metal or metal compound of group VIB (for example molybdenum or tungsten) and at least one metal or metal compound of group VIII (for example cobalt or nickel) of the periodic table. The total concentration of metal oxides of groups VIB and VIII is preferably between 5 and 40% by weight and more preferably between 7 and 30% by weight, and the ratio by weight that is expressed in terms of metal oxide of metal (or metals) of group VIB to metal (or metals) of group VIII is preferably between 1.25 and 20 and more preferably between 2 and 10. In addition, this catalyst can optionally contain phosphorus. The phosphorus content, expressed in concentration of diphosphorus pentaoxide P_2O_5 , will preferably be at most 15%, and more preferably between 0.1 and 15% by weight and very preferably between 0.15 and 10% by weight. It can also contain boron in a B/P ratio that is preferably between 1.02 and 2 (atomic), whereby the sum of the contents of boron (B) and phosphorus (P) that are expressed in terms of oxides are preferably between 5 and 15% by weight.

The first stage generally takes place at a temperature of between 350 and 460°C, preferably between 360 and 450°C, a pressure of at least 2 MPa, preferably at least 3 MPa, an hourly volumetric flow rate of between 0.1 and 5 volumes of feedstock

per volume of catalyst and per hour, preferably between 0.2 and 2 volumes of feedstock per volume of catalyst and per hour and with a quantity of hydrogen of at least 100 normal liters of hydrogen per liter of feedstock, and preferably between 260 and 3000 normal liters of hydrogen per liter of feedstock.

For the conversion stage with the catalyst according to the invention (or second stage), the temperatures are generally greater than or equal to 230°C, often between 300°C and 480°C, and preferably between 330°C and 440°C. The pressure is generally greater than 5 MPa and preferably greater than 7 MPa. The quantity of hydrogen is at least 100 liters of hydrogen per liter of feedstock and preferably between 200 and 3000 liters of hydrogen per liter of feedstock. The hourly volumetric flow rate is preferably between 0.15 and 10 volumes of feedstock per volume of catalyst and per hour.

Under these conditions, the catalysts of this invention have a better conversion activity than the commercial catalysts.

The following examples illustrate this invention without, however, limiting its scope.

Example 1: Preparation of a Substrate that Contains a Zeolite Y
(According to the Invention)

A hydrocracking catalyst substrate that contains a zeolite Y was produced in a large quantity to be able to prepare different catalysts based on the same substrate. For this purpose, 20.5% by weight of a dealuminified zeolite Y with a crystalline parameter that is equal to 2.429 nm and an overall $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 30.4 and a framework $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 58 [calculated according to the so-called Fichtner-Schmittler correlation (in Cryst. Res. Tech. 1984, 19, K1)] is used that is mixed with 79.5% by weight of a matrix that consists of ultrafine tabular boehmite or alumina gel that is marketed under the name SB3 by the Condéa Chemie GmbH [Condea Chemistry GmbH] Company. This powder mixture was then mixed with an aqueous solution that contains nitric acid at 66% by weight (7% by weight of acid per gram of dry gel) then mixed for 15 minutes. At the end of this mixing, the paste that is obtained is passed through a die that has cylindrical orifices with a diameter that is equal to 1.4 mm. The extrudates are then dried for one night at 120°C and then calcined at 550°C for 2 hours in moist air that contains 7.5% volume of water. Cylindrical extrudates that have a 1.2 mm diameter and a specific surface area of 223 m²/g and a monomodal pore size distribution that is centered at 10 nm are then obtained. The analysis of the matrix by x-ray diffraction proves that the latter consists of cubic gamma-alumina of low crystallinity and dealuminified zeolite Y.

Example 2: Preparation of a Hydrocracking Catalyst that Contains a Zeolite Y and a Mixed Sulfide Phase (According to the Invention)

The substrate extrudates that contain a dealuminified zeolite Y of Example 1 are impregnated in the dry state by an aqueous solution of a mixture of ammonium heptamolybdate and nickel nitrate, dried for one night at 120°C in air. The contents by weight of oxides of catalyst A that is obtained are indicated in Table 1; it contains in particular 17.1% by weight of zeolite Y with a mesh parameter of 2.429 nm, an overall $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 30.4 and a framework $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 58.

Catalyst A is impregnated by an aqueous solution of niobium oxalate $\text{Nb}(\text{HC}_2\text{O}_4)_5$, oxalic acid and ammonium oxalate. The aqueous solution that contains niobium is prepared from 1330 ml of water in which 33 g of oxalic acid, 37.2 g of ammonium oxalate and 92.3 g of niobium oxalate are dissolved. To prepare the solution, the oxalic acid and ammonium oxalate mixture is dissolved in a first step, and when the solution is clear, said solution is heated to 55°C, and the niobium oxalate is added. Water is then added to obtain 1330 ml of solution. The substrate of Example 1 above is impregnated by the so-called excess-solution method. The 1330 ml of solution is brought into contact with 380 g of catalyst. This makes it possible to deposit about 5% by weight of Nb on the catalyst. At the end of two hours, the extrudates are recovered. The latter are then dried for one night at 120°C in a stream of dry air. Catalyst B that is obtained contains in particular 16.3% by weight of zeolite Y with a mesh parameter of 2.429 nm.

Tabl 1: Characteristics of Catalysts
(After Calcination for 2 Hours at 500°C in Dry Air)

| Catalyst | 0 | 0 | C | D | E | F |
|--|------|------|------|------|------|------|
| Nb ₂ O ₅ (% by weight) | 0 | 4.8 | 4.8 | 4.9 | 4.8 | 4.8 |
| MoO ₃ (% by weight) | 13.5 | 11.8 | 11.8 | 11.6 | 11.3 | 11.2 |
| NiO (% by weight) | 3.1 | 2.8 | 2.8 | 2.9 | 2.85 | 2.8 |
| B ₂ O ₃ (% by weight) | 0 | 0 | 0 | 0 | 1.9 | 1.9 |
| SiO ₂ (% by weight) | 16.0 | 15.2 | 15.3 | 16.8 | 16.5 | 16.4 |
| F (% by weight) | 0 | 0 | 0 | 0 | 0 | 0.99 |
| Y (% by weight) | 17.1 | 16.3 | 16.3 | 15.6 | 15.7 | 15.5 |
| Addition to 100% of for the most part Al ₂ O ₃ (% by weight) | 67.4 | 65.3 | 65.3 | 63.8 | 62.7 | 61.9 |

Catalysts A and B that are prepared above have been sulfurized in an autoclave under autogenous pressure in the presence of CS₂. For 100 g of catalyst, 20 ml of CS₂ is added to the autoclave, it is closed and heated to 400°C for 10 hours. The internal pressure is then about 4 MPa. This sulfurization is referred to as S1.

Other aliquots of catalysts A and B that are prepared above have been sulfurized in a fixed-bed reactor with a catalyst that has been flushed by a gas stream that contains 15% H₂S in

nitrogen at atmospheric pressure. For 5 g of catalyst, 2 liters of the mixture is passed per hour, and the catalyst is heated to a temperature of 600°C for 6 hours. This sulfurization is referred to as S2.

Analysis by the EXAFS technique is then initiated at threshold K of niobium with synchrotron radiation between 18850 and 19800 eV by measuring the intensity that is absorbed by a powder sample that is deposited on adhesive tape. It makes it possible to determine the interatomic distances. Distances R2 that are measured (in angstrom, $1 \text{ \AA} = 10^{-10} \text{ m}$) by EXAFS for the samples of catalysts A and B that are sulfurized respectively by method S1 and by method S2 are recorded in Table 2.

Table 2

| Catalyst that is Sulfurized by Method S1 | R2 (\AA) | Catalyst that is Sulfurized by Method S2 | R2 (\AA) |
|--|---------------------|--|---------------------|
| B-S1 | 3.21 | B-S2 | 3.21 |
| C-S1 | 3.33 | C-S2 | 3.33 |
| D-S1 | 3.20 | D-S2 | 3.21 |
| E-S1 | 3.21 | E-S2 | 3.21 |
| F-S1 | 3.20 | F-S2 | 3.21 |

Example 3: Preparation of Hydrocracking Catalysts that Contain a Zeolite Y and an Element of Group VB (Not According to the Invention)

A hydrocracking catalyst that contains a zeolite Y and niobium has been produced. This preparation is carried out by co-mixing an ultrafine tabular boehmite mixture or alumina gel that is marketed under the name SB3 by the Condéa Chemie GmbH, a dealuminified zeolite Y with a crystalline parameter that is equal to 2.429 nm and an overall $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 30.4 and a framework $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 58 [calculated according to the so-called Fichtner-Schmittler correlation (in Cryst. Res. Tech. 1984, 19, K1)], of nickel nitrate, niobium pentoxide and ammonium heptamolybdate. To form the paste, these sources are used to obtain a catalyst that contains 16.5% by weight of zeolite Y, 63% by weight of alumina, 13% by weight of molybdenum oxide, 3% by weight of nickel oxide, and 5% by weight of niobium oxide. At the end of this mixing, the paste that is obtained is passed through a die that has cylindrical orifices with a diameter that is equal to 1.4 mm. The extrudates are then dried for one night at 120°C and then calcined at 550°C for 2 hours in moist air that contains 7.5% volume of water. Catalyst C is obtained in the form of cylindrical extrudates with a 1.2 mm diameter whose contents are indicated in Table 1.

Catalyst C that is prepared above is then sulfurized according to method S1 of Example 2 in an autoclave under autogenous pressure in the presence of CS_2 . Another aliquot of catalyst C that is prepared above is sulfurized according to

method S2 of Example 2 in a fixed-bed reactor with a catalyst that is flushed by a gas stream that contains 15% of H_2S in nitrogen at atmospheric pressure. The analysis of these sulfurized catalysts is then initiated by the EXAFS technique as indicated in Example 1. Distances R2 that are measured by EXAFS for samples C-S1 and C-S2 that are sulfurized respectively by method S1 and by method S2 are recorded in Table 2.

Regardless of the sulfurization method, Table 2 notes clearly that the catalysts that contain both niobium and prepared molybdenum according to the invention have an R2 metal-metal distance of the sulfide phase that is less than that of catalyst C. The value of R2 of 3.33 Å for catalyst C indicates that in this catalyst, the niobium is in the form of an NbS_2 phase that is identical to that of a catalyst that would contain only niobium itself. The R2 metal-metal distance of 3.20 Å that is midway between the value of NbS_2 and MoS_2 indicates the presence of a mixed sulfide phase of niobium and molybdenum in catalyst B.

Example 4: Preparation of Hydrocracking Catalysts that Contain a Zeolite Y and a Mixed Sulfide Phase (According to the Invention)

Catalyst A was then impregnated by an aqueous solution that contains a Rhodorsil EP1 silicone emulsion (Rhone-Poulenc). After maturation at ambient temperature in a water-saturated atmosphere, the impregnated extrudates are then dried for one night at 120°C. Catalyst A1 is obtained.

We impregnated the catalyst A sample by an aqueous solution that contains ammonium biborate and the Rhodorsil EP1 silicone

emulsion (Rhône-Poulenc). After maturation at ambient temperature in a water-saturated atmosphere, the impregnated extrudates are dried for one night at 120°C. Catalyst A2 is thus obtained.

Catalysts A1 and A2 are then impregnated by an aqueous solution of niobium oxalate $\text{Nb}(\text{HC}_2\text{O}_4)_5$, oxalic acid and ammonium oxalate. The aqueous solution that contains niobium is prepared from 1330 ml of water in which 33 g of oxalic acid, 37.2 g of ammonium oxalate and 92.3 g of niobium oxalate are dissolved.

To prepare the solution, the oxalic acid and ammonium oxalate mixture is dissolved in a first step and when the solution is clear, said solution is heated to 55°C, and niobium oxalate is added. Water is then added to obtain 1330 ml of solution. Catalysts A1 and A2 are impregnated by the so-called excess-solution method. The 1330 ml of solution are brought into contact with 380 g of catalyst. This makes it possible to deposit about 5% by weight of Nb on the catalyst. At the end of two hours, the extrudates are recovered. The latter are then dried for one night at 120°C in a stream of dry air. Catalyst D is obtained from catalyst A1, and it contains in particular Nb and silicon. Catalyst E is obtained from catalyst A2, and it contains in particular Nb, silicon and boron.

Fluorine is then added to catalyst E by impregnation of a dilute hydrofluoric acid solution to deposit about 1% by weight of fluorine. After drying for one night at 120°C under dry air, catalyst F is obtained.

The characteristics of catalysts D, E and F are summarized in Table 1. Catalysts D, E and F that are prepared above are then sulfurized according to method S1 of Example 2 in an autoclave under autogenous pressure in the presence of CS_2 . Catalysts D, E and F that are prepared above are also sulfurized according to method S2 of Example 2 in a fixed-bed reactor with a catalyst that is flushed by a stream of gas than contains 15% of H_2S in nitrogen at atmospheric pressure.

Analysis by the EXAFS technique is then initiated with these catalysts according to the method that is indicated in Example 1. Distances R2 that are measured by EXAFS for samples D, E, and F that are sulfurized respectively by method S1 and by method S2 are recorded in Table 2. Distance R2 of 3.20 Å and 3.21 Å that is measured for catalysts D, E and F indicates the existence of a mixed sulfide phase of niobium and molybdenum.

**Example 5: Comparison of Hydrocracking Catalysts of a Partially
Converted Vacuum Gas Oil**

The catalysts whose preparations are described in the preceding examples are used under moderate-pressure hydrocracking conditions on a petroleum feedstock whose main characteristics

are as follows:

| | |
|--------------------------|-------|
| Density (20/4) | 0.921 |
| Sulfur (% by weight) | 2.46 |
| Nitrogen (ppm by weight) | 1130 |
| Simulated distillation | |
| Starting point | 365°C |
| 10% point | 430°C |
| 50% point | 472°C |
| 90% point | 504°C |
| Final point | 539°C |
| Pour point | +39°C |

The catalytic test unit comprises two fixed-bed reactors with ascending circulation of the feedstock ("up-flow"). Into the first reactor, the one in which the feedstock passes first, are introduced the catalyst of first hydrotreatment stage HtH548 that is sold by the Procatalyse Company and that comprises an element of group VI and an element of group VIII that are deposited on alumina. Into the second reactor, the one in which the feedstock passes last, is introduced a hydrocracking catalyst that is described above. Into each of the reactors is introduced 40 ml of catalyst. The two reactors operate at the same temperature and at the same pressure. The operating conditions

of the test unit are as follows:

| | |
|-------------------------|-----------------------|
| Total pressure | 5 MPa |
| Hydrotreatment catalyst | 40 cm ³ |
| Hydrocracking catalyst | 40 cm ³ |
| Temperature | 400°C |
| Hydrogen flow rate | 20 l/h |
| Feedstock flow rate | 40 cm ³ /h |

The two catalysts undergo an in-situ sulfurization stage before reaction. We note that any in-situ or ex-situ sulfurization method is suitable. Once the sulfurization is carried out, the feedstock that is described above can be transformed.

The catalytic performance levels are expressed by gross conversion at 400°C (CB), by coarse selectivity of middle distillates (SB) and by conversions of hydrodesulfurization (HDS) and hydrodenitrating (HDN). These catalytic performance levels are measured on the catalyst after a stabilization period, generally at least 48 hours, has elapsed.

Gross conversion CB is assumed to be equal to:

$CB = \% \text{ by weight of } 380^{\text{less}} \text{ of the effluent,}$

whereby the fraction 380^{less} of the effluent means the portion of the effluent that boils below 380°C.

Coarse selectivity SB of middle distillates is assumed to be equal to:

$SB = 100 \times \text{weight of the fraction (150°C-380°C)} / \text{weight of the fraction } 380^{\text{less}} \text{ of the effluent}$

The HDS hydrodesulfurization conversion is assumed to be equal to:

$$\text{HDS} = (S_{\text{initial}} - S_{\text{effluent}}) / S_{\text{initial}} * 100 = (24600 - S_{\text{effluent}}) / 24600 * 100$$

The HDN hydrodenitrating conversion is assumed to be equal to:

$$\text{HDN} = (N_{\text{initial}} - N_{\text{effluent}}) / N_{\text{initial}} * 100 = (1130 - N_{\text{effluent}}) / 1130 * 100$$

In Table 3 below, we recorded gross conversion CB at 400°C, coarse selectivity SB, hydrodesulfurizing conversion HDS and hydrodenitrating conversion HDN for the four catalysts.

Table 3: Catalytic Activities of the Partial Hydrocracking Catalysts at 400°C

| | | CB (% by weight) | SB (%) | HDS (%) | HDN (%) |
|---|------------------------------|------------------------|-----------|------------|------------|
| A | NiMo/Y | 47.1 | 76.0 | 97.0 | 94.2 |
| B | NiMoNb/Y | 47.3 | 79.4 | 98.1 | 95.6 |
| C | NiMoNb/Y (for comparison) | 47.8 | 75.8 | 97.9 | 95.3 |
| D | NiMoNbSi/Y | 47.2 | 79.4 | 98.4 | 96.2 |
| E | NiMoNbBSi/Y | 47.3 | 79.6 | 98.5 | 96.8 |
| F | NiMoNbBSiF/Y | 47.6 | 79.7 | 98.7 | 97.0 |

The results of Table 3 show that the presence of a mixed sulfide phase of molybdenum-niobium provides an improvement of the performance levels of the catalyst of HDS, HDN. This is due to the better activity of the mixed sulfide phase compared to that of catalyst C that does not contain this phase. The conversion performance level is equivalent while the coarse selectivity of middle distillates is improved due to a more hydrogenating phase. When a promoter that is selected from group P, B, Si, optionally fluorine, is added, a slight improvement of the conversion and an improvement of selectivity are observed. The catalysts with a dealuminified zeolite Y base of the invention that contain a mixed sulfide phase that contains at least one element of group VB and at least one element of group VIB are therefore particularly advantageous for partial hydrocracking of vacuum distillate-type feedstock that contains nitrogen at a moderate hydrogen pressure. They are also improved by the presence of at least one promoter that is selected from group P, B, Si, F.

Example 6: Comparison of Catalysts for Hydrocracking a High-Conversion Vacuum Gas Oil

The catalysts whose preparations are described in the examples above are used under high-conversion hydrocracking conditions (60-100%). The petroleum feedstock is a hydrotreated

vacuum distillate whose main characteristics are as follows:

| | |
|--------------------------|-------|
| Density (20/4) | 0.869 |
| Sulfur (% by weight) | 502 |
| Nitrogen (ppm by weight) | 10 |
| Simulated distillation | |
| Starting point | 298°C |
| 10% point | 369°C |
| 50% point | 427°C |
| 90% point | 481°C |
| Final point | 538°C |

This feedstock was obtained by hydrotreatment of a vacuum distillate on an HR360 catalyst that is sold by the Procatalyse Company that comprises an element of group VI and an element of group VIII that are deposited on alumina.

0.6% by weight of aniline and 2% by weight of dimethyl disulfide are added to the feedstock to simulate partial pressures of HS_2 and NH_3 that are present in the second hydrocracking stage. The feedstock that is thus prepared is injected into the hydrocracking test unit that comprises a fixed-bed reactor with ascending circulation of the feedstock ("up-flow"), into which is introduced 80 ml of catalyst. The catalyst is sulfurized by an n-hexane/DMDs + aniline mixture to 320°C. We note that any in-situ or ex-situ sulfurization method is suitable. Once the sulfurization is carried out, the feedstock that is described above can be transformed. The operating

conditions of the test unit are as follows:

| | |
|---------------------|-----------------------|
| Total pressure | 9 MPa |
| Catalyst | 80 cm ³ |
| Temperature | 360-420°C |
| Hydrogen flow rate | 80 l/h |
| Feedstock flow rate | 80 cm ³ /h |

The catalytic performance levels are expressed by the temperature that makes it possible to reach a gross conversion level of 70% and by coarse selectivity of middle distillates 150-380°C. These catalytic performance levels are measured in the catalyst after a stabilization period, generally at least 48 hours, has elapsed.

Gross conversion CB is assumed to be equal to:

CB = % by weight of 380^{less} of the effluent.

Coarse selectivity SB of a middle distillate is assumed to be equal to:

SB = 100* weight of the fraction (150°C-380°C)/weight of the fraction 380^{less} of the effluent

The reaction temperature is set to reach a gross conversion CB that is equal to 70% by weight. In Table 4 below, we recorded the reaction temperature and the coarse selectivity for the catalysts that are described in Tables 1 and 2.

Table 4

**Catalytic Activities of High-Conversion Hydrocracking NiMo
and NbNiMo Catalysts (70%)**

| | | T(°C) | SB |
|---|---------------------------|-------|------|
| A | NiMo/Y | 376 | 63.7 |
| B | NiMoNb/Y | 374 | 65.3 |
| C | NiMoNb/Y (for comparison) | 374 | 63.9 |
| D | NiMoNbSi/Y | 373 | 65.9 |
| E | NiMoNbBSi/Y | 372 | 66.9 |
| F | NiMoNbBSiF/Y | 370 | 66.9 |

By comparison with catalyst C, the presence of a molybdenum-niobium sulfide mixed phase in the catalyst that contains the dealuminified zeolite Y of the invention makes it possible to improve the selectivity significantly thanks to the better quality of the hydro-dehydrogenating function that consists of the mixed sulfide phase.

It is also observed that by adding Si, B, and/or F into the catalyst that contains the mixed sulfide phase, the improvement of the selectivity is maintained while increasing the conversion activity, which is reflected by a reduction of the reaction temperature that is necessary to reach 70% conversion.

The catalysts of the invention that contain a mixed sulfide phase that comprises at least one element of group VB and at least one element of group VB are therefore particularly advantageous for high-conversion hydrocracking of vacuum, distillate-type feedstock.